Calculation of Excess Adiabatic Compressibility from Ternary Liquid Experimental Data

Vladimír Hanta[1], Lenka Morávková[2]

[1]Department of Computing and Control Engineering, Faculty of Chemical Engineering, Institute of Chemical Technology Prague, Technická 5, 166 28 Prague 6, Czech Republic, phone: +420 2 2044 4212, fax: +420 2 2044 5053, e-mail: hantav@vscht.cz
[2]Department of Separation Processes, Institute of Chemical Process Fundamentals, Rozvojová 2/135, 165 02 Prague 6, Czech Republic, phone: +420 220 390 133, fax: +420 220 920 661, e-mail: moravkova@icpf.cas.cz

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Introduction

Matlab program ExAdComp3, ver. 3.08, calculates excess adiabatic compressibility for ternary liquid mixtures. The mixture adiabatic compressibility is calculated from the measured density and speed of sound in the mixture. Values of ideal adiabatic compressibility are computed from the Kiyohara-Benson equation depending on temperature, ideal volume fractions of mixture and adiabatic compressibility, molar volume, coefficients of thermal expansion and isobaric molar heat capacity of pure components. The modified Redlich-Kister equation is used for data fitting. This data model can optionally contain different numbers of binary and ternary constants. The optimization is carried out using the least squares method. All calculations are performed in computational environment of the Matlab system with help of Optimization Toolbox functions.

Brief theoretical fundamentals

Values of the adiabatic compressibility, κ_S, were evaluated by the Laplace equation [1] using experimental densities, ρ, and speed of sound, u, as follows

$$\kappa_S = 1/(\rho\, u^2).$$

Values of the excess adiabatic compressibility, κ_S^E, are determined from the difference between experimental adiabatic compressibility, κ_S, and the ideal compressibility, κ_S^{id}

$$\kappa_S^E = \kappa_S - \kappa_S^{id}.$$

The definition of the ideal adiabatic compressibility, κ_S^{id}, is described in detail in [2] as follows

$$\kappa_S^{id} = \sum_{i=1}^{N} \phi_i \left(\kappa_{S,i}^0 + T\, V_i^0 \left(\alpha_{p,i}^0\right)^2 / C_{p,i}^0\right) - T \left(\sum_{i=1}^{N} x_i\, V_i^0\right) \left(\sum_{i=1}^{N} \phi_i\, \alpha_{p,i}^0\right)^2 / \sum_{i=1}^{N} x_i\, C_{p,i}^0,$$

where N is number of components, ϕ_i denotes volume fraction of the component i in the mixture and x_i is mole fraction of the component i. Temperature is denoted as T, and $\kappa_{S,i}^0$, V_i^0, $\alpha_{p,i}^0$, and $C_{p,i}^0$ are respectively the adiabatic compressibility, molar volume, coefficient of thermal expansion, and molar heat capacity for the pure component i.

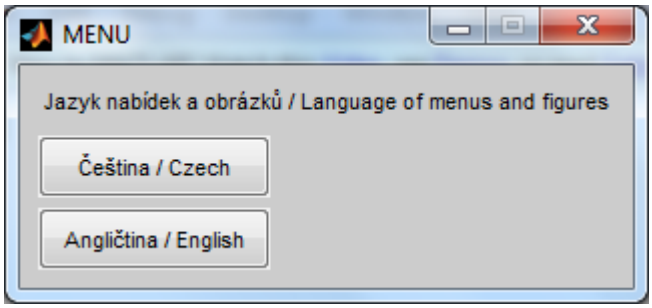
Complete volumetric data of the ternary system processed as well as its binary sub-systems were correlated simultaneously by the Redlich–Kister equation [3]

$$\kappa_S^E = \left[\sum_{i<j}^{N} x_i x_j \sum_{k=0}^{n} A_{(ij)k}\left(x_i - x_j\right)^k\right] + x_1 x_2 x_3 (B_0 + B_1 x_1 + B_2 x_2 + B_3 x_1^2 + B_4 x_1 x_2 + B_5 x_2^2)$$

where $A_{(ij)k}$ are binary and B_m ternary adjustable parameters. The number of parameters, $A_{(ij)k}$ and B_m, which are necessary to represent experimental data properly depends on molecular complexity of the solution (i.e., the shape of the curve of excess molar volume versus composition) as well as on a number of experimental points and on their quality. An advantage of this equation is that it is linear in parameters, which can be evaluated easily using finite linear regression methods that do not require a first approximation and provide a straightforward solution.

Procedure of digital processing of measured data

- **selection of the language of menus, figures and information messages**



- **entering the name of the data file and reading the data**

```
Input data file
***************

Enter the name of the data file: testdata


Data file testdata.xls was successfully opened!!!
```

- **structure of mixture components data (worksheet Constants)**

Mixture components			
$Comp_1$	**$Comp_2$**	**$Comp_3$**	
Molar masses			**Temperature**
M_1	***M_2***	***M_3***	***T***
114,228 52	92,138 42	74,121 60	298,15
$g.mol^{-1}$	$g.mol^{-1}$	$g.mol^{-1}$	K
Densities			
ρ_1	ρ_2	ρ_3	
0,687 680	0,862 190	0,805 730	
$g.cm^{-3}$	$g.cm^{-3}$	$g.cm^{-3}$	
Molar heat capacities			
C_{P1}	**C_{P2}**	**C_{P3}**	
238,57	157,13	177,12	
$J.K^{-1}.mol^{-1}$	$J.K^{-1}.mol^{-1}$	$J.K^{-1}.mol^{-1}$	
Coefficients of thermal expansion			
α_{P1}	α_{P2}	α_{P3}	
0,001 211	0,001 081	0,001 034	
K^{-1}	K^{-1}	K^{-1}	

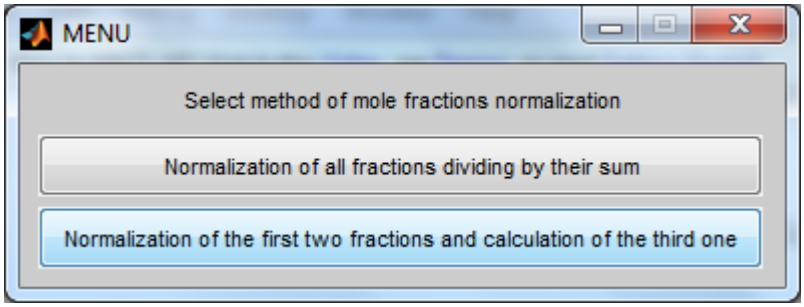
- **reading mixture components data**

```
Reading input data
******************

Names of three components successfully read!!!
1. component: Comp1
2. component: Comp2
3. component: Comp3

Molar masses of three components successfully read!!!
Molar mass of 1. component: 114.2285 g/mol
Molar mass of 2. component: 92.1384 g/mol
Molar mass of 3. component: 74.1216 g/mol

Densities of three components successfully read!!!
Density of 1. component: 0.68768 g/cm^3
Density of 2. component: 0.86219 g/cm^3
Density of 3. component: 0.80573 g/cm^3

Molar heat capacities of three components successfully read!!!
Molar heat capacity of 1. component: 238.57 J/K/mol
Molar heat capacity of 2. component: 157.13 J/K/mol
Molar heat capacity of 3. component: 177.12 J/K/mol

Thermal expansivity coefficients of three components successfully read!!!
Thermal expansivity coefficient of 1. component: 0.001211 1/K
Thermal expansivity coefficient of 2. component: 0.001081 1/K
Thermal expansivity coefficient of 3. component: 0.001034 1/K

Measurement temperature successfully read!!!
Measurement temperature: 298.15 K
```

- **reading measured values of density and speed of sound**

```
Measured values of density and speed of sound in ternary mixtures successfully read!!!
116 measured points read!!!
```

- **selection of method of mole fractions normalization**



- **structure of experimental measured density and speed of sound data (a part of the worksheet Data)**

$Comp_1$	$Comp_2$	$Comp_3$	Temperature	298,15 K
Molar fractions			Density	Speed of sound
x_1	x_2	x_3	ρ	u
-	-	-	g.cm^{-3}	m.s^{-1}
0,000 00	1,000 00	0,000 00	0,86219	1 305,30
0,046 11	0,953 89	0,000 00	0,84992	1 288,09
0,130 25	0,869 75	0,000 00	0,82904	1 259,07
0,199 86	0,800 14	0,000 00	0,81310	1 237,43
0,261 80	0,738 20	0,000 00	0,79981	1 219,70
0,330 10	0,669 90	0,000 00	0,78608	1 201,88
0,405 14	0,594 86	0,000 00	0,77198	1 183,66
0,459 00	0,541 00	0,000 00	0,76243	1 171,61
0,527 58	0,472 42	0,000 00	0,75093	1 157,30
0,591 04	0,408 96	0,000 00	0,74091	1 145,06
0,665 41	0,334 59	0,000 00	0,72983	1 132,32
0,732 91	0,267 09	0,000 00	0,72039	1 120,35
...	...	...	...	...

- **writing experimental data**

```
Writing experimental data
*************************

Writing data to output MS Excel tables!!!
Wait, data writing may take tens of seconds!!!

Results worksheet added into file testdata.xls !!!

101 rows of measured values written into file testdata.xls successfully!!!
```

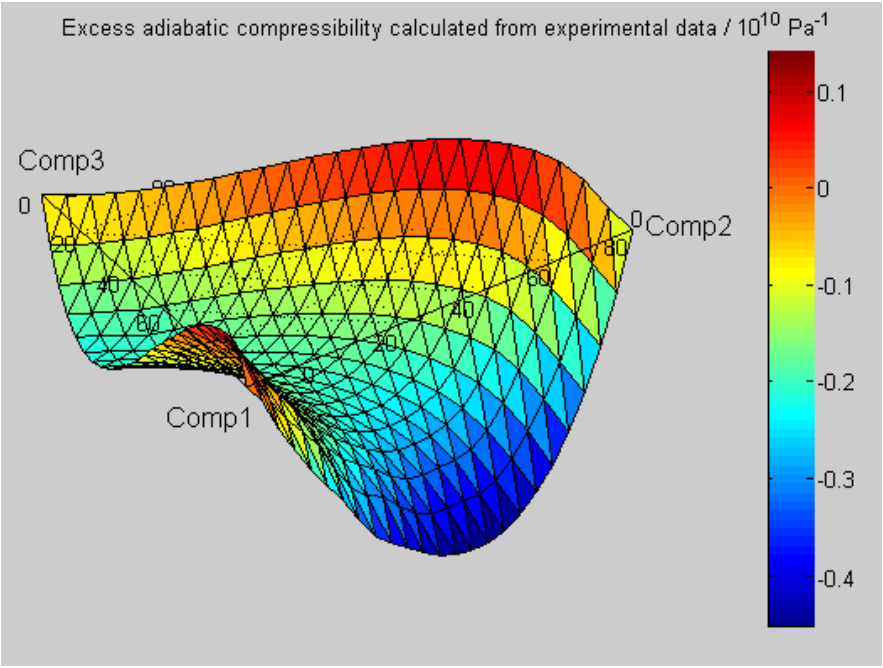
- **written processed density, speed of sound and excess adiabatic compressibility data (part of worksheet Results)**

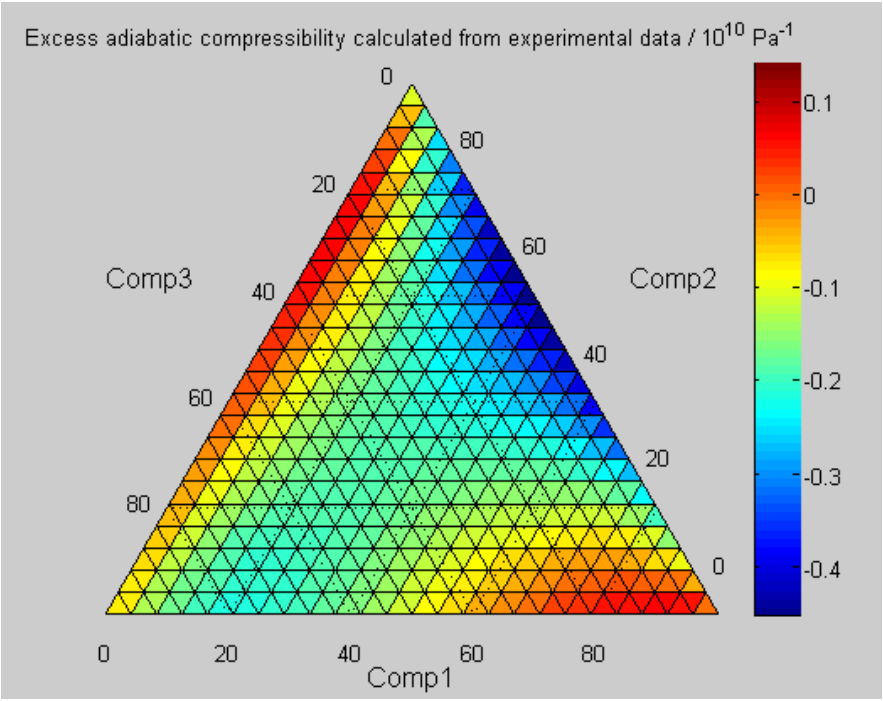
Comp1	Comp2	Comp3	Temperat	298,15				
Mole fractions			Density	Speed of s	Excess adiabatic compressibility			
x1	x2	x3	r	u	kappaES exp			
-	-	-	g/cm3	m/s	1/TPa			
0	0	1	0,805724	1239,917	0			
0	0,026208	0,973792	0,807503	1241,07	0,053107			
0	0,069788	0,930212	0,810419	1242,9	0,326974			
0	0,133437	0,866563	0,814513	1245,433	1,135062			
0	0,190938	0,809062	0,818082	1247,59	2,221243			
0	0,26056	0,73944	0,822263	1250,14	3,824513			
0	0,33909	0,66091	0,826798	1252,897	6,048024			
...	...	...	...	...	...			

- **writing calculated values of excess adiabatic compressibility**

```
Writing calculated excess adiabatic compressibilities
*****************************************************

Writing data to output MS Excel tables!!!
Wait, data writing may take tens of seconds!!!

101 rows of measured values written into file testdata.xls successfully!!!
```

- **visualization of excess adiabatic compressibility**





- **entering parameters of modified Redlich-Kister equation**

```
Parameters of modified Redlich-Kister equation
**********************************************

Enter degrees of Redlich-Kister equation binary parts: 2
Enter degree  of Redlich-Kister equation ternary part: 2
```

- **fitting excess adiabatic compressibility using modified Redlich-Kister equation by means of least squares method**

```
Progress and results of optimization
************************************

Results of calculated data fitting
Sum of error squares          : 4.8255e-03
Maximum error                 : 2.6392e-02
Average error                 : 4.7553e-03
Number of taken iterations    :          17
Number of function evaluations:         288

Optimum reached successfully in     0.7433 s!!!
Change in goal function value is less than 2.2204e-16 !!!
```

- **optimal values of modified Redlich-Kister equation coefficients**

```
Optimum coefficients of modified Redlich-Kister equation
********************************************************

A(1,2)0 = -1.751179
A(1,2)1 =  0.655171
A(1,2)2 = -0.133187
A(1,3)0 = -0.470507
A(1,3)1 =  1.352873
A(1,3)2 = -0.084432
A(2,3)0 =  0.430528
A(2,3)1 =  0.591146
A(2,3)2 =  0.134490
B(0)    =  0.162950
B(1)    = -1.388622
B(2)    = -5.758495
B(3)    =  2.890324
B(4)    =  11.768269
B(5)    =  6.664921
```

- **writing optimal values of modified Redlich-Kister equation coefficient (worksheet Coefficients)**

```
Writing coefficients of modified Redlich-Kister equation
*******************************************************

Writing coefficients to output MS Excel workbook!!!
Wait, data writing may take tens of seconds!!!

Coefficients worksheet added into file testdata.xls !!!

15 optimum coefficients of Redlich-Kister equation successfully written to file testdata.xls !!!
```

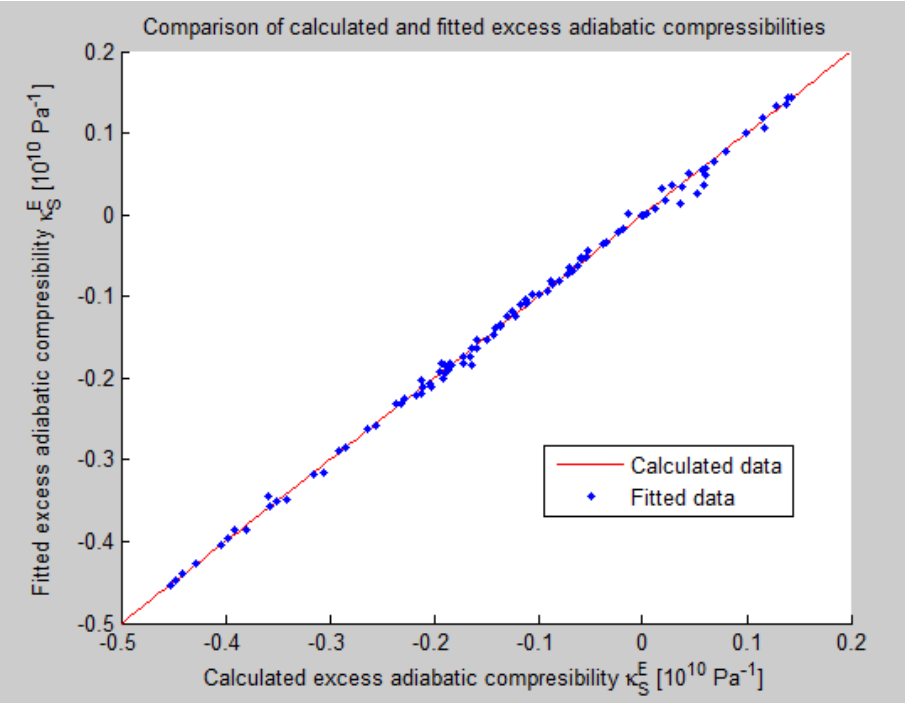
- **written optimum values of modified Redlich-Kister equation (worksheet Coefficients)**

Coefficients of modified Redlich-Kister equation				
binary parts degree		2		
ternary part degree		2		
A(1,2)0	-1,75118			
A(1,2)1	0,655171			
A(1,2)2	-0,13319			
A(1,3)0	-0,47051			
A(1,3)1	1,352873			
A(1,3)2	-0,08443			
A(2,3)0	0,430528			
A(2,3)1	0,591146			
A(2,3)2	0,13449			
B(0)	0,16295			
B(1)	-1,38862			
B(2)	-5,7585			
B(3)	2,890324			
B(4)	11,76827			
B(5)	6,664921			

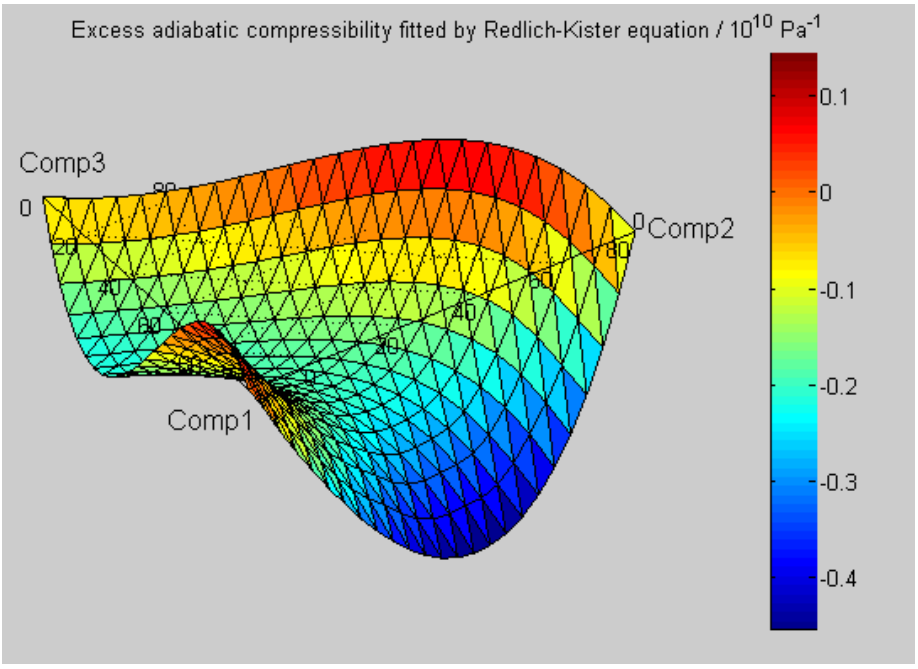
- **writing fitted values of excess molar volumes**

```
Writing fitted excess volumes
*********************************

Writing data to output MS Excel tables!!!
Wait, data writing may take tens of seconds!!!

101 rows of measured values written into file testdata.xls successfully!!!
```

- **graphical comparison of calculated and fitted values of excess adiabatic compressibility**



- **visualization of fitted values of excess molar volumes**



- **written values of excess adiabatic compressibility calculated from experimental data and fitted using modified Redlich-Kister equation (part of worksheet Results)**

Excess adiabatic compressibility	Excess adiabatic compressibility
kappaES exp	kappa ES RKe
1/TPa	1/TPa
0	0
0,053107117	-0,022640805
0,326974164	0,13930651
1,135061742	0,802814628
2,221242621	1,799899408
3,824512967	3,434928982
6,048024082	5,697163198
...	...

References

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[2] Kiyohara, O., Benson, G. C.: Ultrasonic speeds and isentropic compressibilities of n-alkanol + n-heptane mixtures at 298.15 K. *J. Chem. Thermodyn.*, 11, 9, 861–873, 1979.

[3] Morávková, L., Troncoso, J., Machanová, K., Sedláková, Z: Volumetric behaviour of the (2,2,4-trimethylpentane + methylbenzene + butan-1-ol) ternary system and its binary sub-systems within the temperature range (298.15-328.15) K. *J. Chem. Thermodyn.*, 64, 1, 137–150, 2013.